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6. AUTHORS
Dr. Sarah A. Headrick, H. Gene Johnston, Dr. Brian Roos

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Alliant Ammunition and Powder Company
Route 114
PO Box 1
Radford, VA 24143 -

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14. ABSTRACT
The U.S. Army Research Laboratory (ARL) is developing a series of insensitive melt cast explosive formulations to replace the conventional TNT-based fills which fails to meet Insensitive Munitions (IM) requirements. These formulations are based upon a nitrate salt based eutectic mixture called DEMN. These DEMN formulations have previously been demonstrated to have significantly improved IM response, passing 4 out of 5 IM tests in the 155mm M795 artillery projectile. Two components of this DEMN eutectic are the energetic salts, Ethylenediamine

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| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Sarah Headrick |
| U | U | U | SAR | | 19b. TELEPHONE NUMBER |
| | | | | | 540-639-8187 |

## I. Foreword

Composition B is an explosive formulation that has been used for years in bomb fills, grenades and anti-personnel mines. The material consists of RDX, TNT and wax. Although Composition B has been a versatile and generally stable material, there are improvements to be made. First of all, the traditional route to TNT results in an environmentally unfriendly byproduct called "red water". Secondly, the Department of Defense has mandated that all munitions become compliant with Insenstive Munitions (IM) requirements. Insensitive munitions are capable of withstanding accidents, fires or enemy attacks without significant contribution to platform damage. As Composition B filled warheads do not meet IM requirements, largely due to the intrinsic sensitivity of the formulation, replacements for Composition B are being evaluated.[1] In response to this need, ARL has been developing a series of reduced sensitivity melt cast explosive formulations that are based on the nitrate salt containing eutectic mixture, DEMN.[2-5] Two of the components of DEMN are EDDN and DETN. ARL was able to generate the materials in 25 pound batches but larger quantities will be needed for explosive qualification.

## II. List of Figures

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## IV. Statement of the Problem

The U.S. Army Research Laboratory (ARL) is developing a series of insensitive melt cast explosive formulations to replace the conventional TNT-based fills. These formulations are based upon a nitrate salt based eutectic mixture called DEMN. Two components of this DEMN eutectic are the energetic salts, Ethylenediamine Dinitrate (EDDN) and Diethylenetriamine Trinitrate (DETN). The manufacture of these salts was previously conducted at ARL in 25 pound batches, however, for explosive qualification, larger quantities were required. The two DEMN salts, EDDN and DETN were generated at the Radford Army Ammunition Plant (RFAAP) and delivered to ARL for use in the DEMN formulation.

## V. Results

### A. Experimental

The schematic for production of the DEMN salts is given in Figure 1. A photograph of the actual reactor that was used for this project is depicted in Figure 2.

**Figure 1. DEMN Salts Reaction Setup**

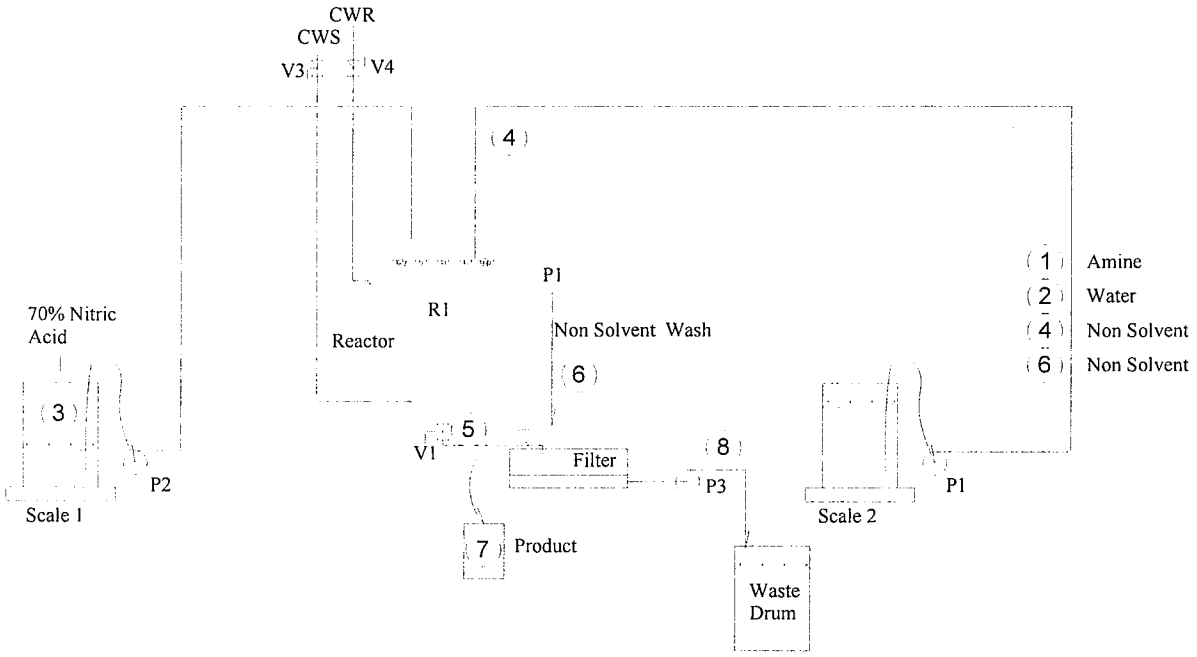
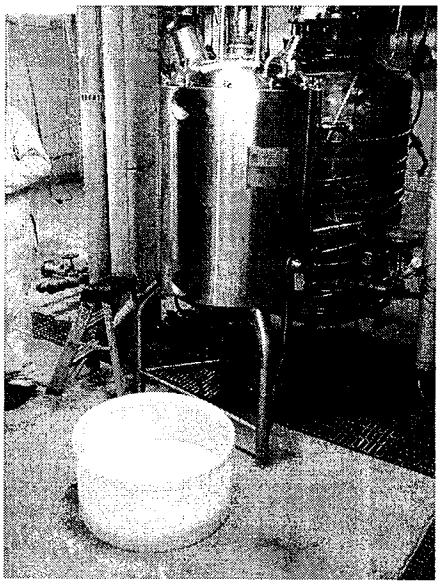



**Figure 2. Buchner Funnel and Reactor for DEMN Salts Reaction**



The general procedure that was utilized is as follows. The starting amine material was pumped into the reactor followed by an appropriate amount of water. This was followed by addition of approximately 70% nitric acid. The acid used was mixed from the two acids acquired in RFAAP's acid manufacturing line. The ammonia oxidation plant (AOP) provides 62% nitric acid and the Nitric Acid Concentrator/Sulfuric Acid Concentrator (NAC/SAC) provides 99% nitric acid. Upon complete addition of the acid, the reaction solution was sampled and tested for acidity. If the desired acidity was not met, either additional acid or amine was added to bring the reaction solution to the desired composition. When the desired result was achieved, the reaction solution was allowed to cool to and a non-solvent was added in order to crystallize the salt. After a crystallization period, the reaction mixture was filtered. The crystals were washed with non-solvent and the material was packed out.

**B. DETN Reaction Results**

DETN was scaled up at RFAAP from an initial 40 lb batch size to the 157 lb batch, the maximum for the reactor that was used. Removal of material from the reactor resulted in plugging of the outlet in the initial reaction. These issues were alleviated when the configuration for removal from the reactor was changed, the crystallization time shortened and the temperature during crystallization was kept higher. These issues are not expected to arise at the next batch size as the improved crystallization techniques will be applied and the reactors in RFAAP's new Pilot Plant have rising stem flush bottom valves that are designed to prevent plugging from occurring.

The analytical results from the DETN reactions are given in Table 2 and the yield information is given in Table 3. All samples conformed to the provided specification of 151 ±2 °C for DSC melt temperature. This is a sign of a very robust and predictable process. The nitric acid content was 0.83% on average and remained consistent for the reactions. This is indicative of a reproducible process. The average solvent content of the un-dried material was found to be 29% and the average residual water content was 3.1%. The percentage of water insoluble material was 0.04% which is very low. The density of the product was 1.56 g/mL which is within the provided specification of 1.58 ± 0.05 g/mL. Final yield information for all DETN reactions completed at RFAAP is given in Table 3.

**Table 1. DETN Analytical Results**

| Rxn # | Batch Size | Rxn sol'n pH | DSC Melt (°C) | % Solvent | % $H_2O$ | % $HNO_3$ | % $H_2O$ Insol. | Density (g/mL) |
|---|---|---|---|---|---|---|---|---|
| 1 | 40 lb | 3.70 | 150.8 | 29.11 | 2.04 | 0.86 | 0.05 | 1.56 |
| 2 | 40 lb | 3.60 | 151.5 | 30.00 | 2.01 | 0.75 | - | - |
| 3 | 52 lb | 4.15 | 151.2 | 30.63 | 2.95 | 0.84 | - | - |
| 4 | 104 lb | 2.12 | 152.4 | 30.78 | 3.54 | 0.87 | - | - |
| 5 | 157 lb | 4.13 | 152.0 | 27.70 | 3.62 | 0.82 | - | - |
| 6 | 157 lb | 4.27 | 151.8 | 27.13 | 4.48 | 0.88 | - | - |
| Composite | - | - | - | - | - | - | 0.04 | 1.56 |

**Table 2. Yield Information for DETN Reactions**

| Rxn # | Total Wet Wt. (lb) | Total Dry Wt. (lb) | % Yield* |
|---|---|---|---|
| 1 | 56.7 | 39.0 | 98 |
| 2 | 59.1 | 40.2 | 101 |
| 3 | 76.6 | 49.4 | 95 |
| 4 | 158.4 | 104.1 | 100 |
| 5 | 221.8 | 152.4 | 97 |
| 6 | 229.2 | 156.8 | 100 |

*Yields based on calculated dry weights resulting from solvent, water and acid content analyses.

The DETN reactions were extremely high-yielding and the average yield was 98.7%. This was in line with average yield of 97.5% that was acquired previously at ARL. In addition, the data showed that while the pH of the solutions prior to crystallization ranged from 2.12 to 4.27, the DSC melt range only varied by 1.6 °C. As DSC melt is an indicator of purity, this implies that the material was pure on a consistent basis. Therefore, some variation in the acidity of the reaction solution is allowable and will not affect the final product quality. This is indicative of a process that is quite robust. Robustness is a desirable characteristic for reactions of this kind as it allows the process to be more scalable. Also, the specification given for DSC melt was 152 ±2 °C and this specification was met for every batch. This too, is an indication of a robust process. The average solvent content was found to be 29% and the average water content was 3.1%. This was a desirable range for these parameters as the final material was shipped wet.

### C. EDDN Reaction Results

EDDN was scaled up from an initial 49 lb scale to the 147 lb batch size. Lessons learned from the DETN reactions were applied to EDDN and made the process proceed more efficiently. The time to complete the first small scale reaction for EDDN was 46% less than that of the first DETN reaction which will yield a significant cost savings in the future. From the onset, the crystallization procedure was modified and only minor plugging of the reactor in the first reaction which was reduced as the process was optimized. As mentioned previously, this concern will be eliminated when the materials are manufactured in RFAAP's new pilot plant. Analytical data for EDDN is given in Table 5 and final yield data is in Table 6. The DSC melt temperatures were all within the provided specification of 188 ±2 °C. The average solvent content for the material was 31% while the average water content was 3.3%. The average nitric acid content of the material was 0.07% and remained consistent through the process. Finally, the water-insoluble content was 0.02% for the composite sample. The density of the material was 1.60 g/mL which was within the specification of 1.59 ± 0.05 g/mL.

**Table 3. EDDN Analytical Data**

| Rxn | Batch Size | Rxn sol'n pH | DSC Melt (°C) | % Solvent | % $H_2O$ | % $HNO_3$ | % $H_2O$ Insol. | Density (g/mL) |
|---|---|---|---|---|---|---|---|---|
| 1 | 49 lb | 5.98 | 187.6 | 33.95 | 2.79 | 0.06 | - | - |
| 2 | 65 lb | 4.92 | 188.2 | 28.88 | 4.90 | 0.06 | - | - |
| 3 | 104 lb | 6.14 | 187.9 | 34.92 | 3.07 | 0.08 | - | - |
| 4 | 157 lb | 6.10 | 188.1 | 27.73 | 3.70 | 0.08 | - | - |
| 5 | 157 lb | 6.29 | 187.9 | 28.73 | 4.80 | 0.08 | - | - |
| 6 | 65 lb | 5.11 | 188.2 | 29.97 | 0.44 | 0.07 | - | - |
| Composite | - | - | - | - | - | - | 0.02 | 1.60 |

**Table 4. Yield Information for EDDN Reactions**

| Rxn # | Total Wet Wt. (lb) | Total Dry Wt. (lb) | % Yield* |
|---|---|---|---|
| 1 | 64.2 | 40.6 | 83 |
| 2 | 82.9 | 54.9 | 85 |
| 3 | 135.1 | 83.8 | 81 |
| 4 | 205.8 | 141.1 | 90 |
| 5 | 207.2 | 137.7 | 88 |
| 6 | 91.1 | 63.4 | 98 |

*Yields based on calculated dry weights resulting from solvent, water and acid content analyses.

The ATK EDDN reactions were slightly lower-yielding than the DETN reactions with an average yield of 88% in comparison to ARL's previous yield of 91%. The true yield, however, was probably

not significantly different than that of the DETN synthesis as some of the EDDN plated out onto the surfaces of the reactor vessel. For expediency of this project, a plan was not developed to minimize or recover this material. In the future, a process will be put in place to recover this material. One possible solution would be to simply dissolve the material in the water and amine solution for the next reaction. The lost material would be recovered with the next reaction and there would always be some material that remained in the vessel, but this amount of material would only be lost on the first of a series of reactions. Similarly to DETN, the EDDN purity was consistently high. The specification for DSC melt was 188 ±2 °C. The results showed that the greatest deviation from the melt was 0.4 °C which is very good. This indicates that this process reliably provides a high purity product.

**D. Conclusions**

The initial scale up of EDDN and DETN were completed at ATK's RFAAP with few issues. More than 500 lbs of each material has been made and conformed to the required purity specifications.

Upon completion of this initial work, there are areas identified for improvement in the future. First, a significant cost savings can be achieved through the elimination of the crystallizing non-solvent. There are several methods that are being considered to eliminate this costly component of the process. One such method is to use a prilling tower to obtain the dry, crystallized material directly from the aqueous reaction solution. A second method is to crystallize the salt directly from the aqueous solutions. Initial material can be crystallized from the aqueous solution and after filtration; the solution can be concentrated to allow more material to crystallize. Plans are in place to complete a small scale study of these options to ensure that product quality could be maintained with these process changes. Of particular concern is to confirm that although solvent was used in this process to wash the material, it is not necessary for optimal product quality.

A second area to improve is the plating of EDDN onto the walls of the reactor. Several options for this improvement have been identified. The simple solution is to leave the material in the reactor and allow it to dissolve in the amine and water for the next reaction. It is also possible that this may not be an issue at all. The reactor used for this work was unlined stainless steel and it is possible that the crystals will not stick to the walls in the glass-lined reactors at the pilot plant.

A final improvement that will be explored is generation of the two salts simultaneously. The starting amines will be fed to the reactor in the desired DEMN formulation ratio and the materials could be generated simultaneously. This would eliminate the processing time that is required for mixing the materials prior to addition to the formulation and therefore lower cost.

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